IC bureau of mines
information circular 8007

HEAVY LIQUIDS AND PROCEDURES FOR LABORATORY SEPARATION OF MINERALS

By J. S. Browning

UNITED STATES DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
(1961)

This publication has been cataloged as follows:

Browning, James Scott

Heavy liquids and procedures for laboratory separation of minerals. [Washington] U.S. Dept. of the Interior, Bureau of Mines [1961]

14 p. illus. 26 cm. (U.S. Bureau of Mines. Information circular 8007)

Based on work done in cooperation with the University of Alabama.

Bibliographical footnotes.

1. Mineralogy. I. Title. II. Title: Separation of minerals. (Series)

[TN23.U71 no. 8007] 622.06173

U.S. Dept. of the Int. Library.

CONTENTS

Page

Introduction and Summary.. 1
Applicability of sink-float separations..................... 2
Basic apparatus required for laboratory sink-float separations.. 2
Test procedures.. 4
  Beaker separations.. 5
  Funnel separations.. 5
  Centrifuge separations.................................. 6
Sink-float liquids--their properties and recovery.......... 6
  Water.. 6
  Carbon tetrachloride..................................... 7
  Bromoform... 8
  Acetylene tetrabromide................................. 8
  Methylene iodide... 10
  Thallium formate... 10
  Thallium-malonate-formate............................ 11
  Cargille heavy liquids.................................... 12
Difficulties encountered in sink-float separations......... 13
Safety precautions for handling sink-float liquids......... 14

ILLUSTRATIONS

Fig.

1. Equipment for laboratory sink-float separations....... 3
2. Typical sink-float separations in beakers, separatory funnels, and centrifuge tubes............ 4
3. Specific gravity of mixtures of carbon tetrachloride and benzene at 25° C........................ 7
4. Specific gravity of mixtures of bromoform and carbon tetrachloride at 25° C........................ 9
5. Specific gravity of mixtures of acetylene tetrabromide and carbon tetrachloride at 25° C........... 10
6. Specific gravity of mixtures of thallium formate and water at 90° C.................................. 11
7. Specific gravity of mixtures of thallium-malonate-formate and water at 90° C........................... 12

Original from THE OHIO STATE UNIVERSITY

HEAVY LIQUIDS AND PROCEDURES FOR LABORATORY SEPARATION OF MINERALS[1]

by

J. S. Browning[2]

INTRODUCTION AND SUMMARY

The physical properties and specific gravity ranges of various liquids and salt solutions used for laboratory sink-float separations of rocks or minerals are presented. The test equipment and techniques employed by the Bureau of Mines in making sink-and-float separations of particles as coarse as 3 inches to as fine as 400 mesh are described. Also discussed are methods of recovering and reclaiming the liquids or salts from the minerals and wash solutions, as well as the hazards encountered and precautions to be followed while working with the materials.

The laboratory use of various liquids for separating minerals of different specific gravities has been recognized for many years. During this time, laboratory sink-float procedures have proven their utility as a rapid and moderately accurate means for determining the mineral content of ores, test products, and plant products in certain nonmetallic concentrating operations, such as those producing mica, spodumene, kyanite, and so forth. These procedures also have been used as analytical tools for determining the mineral content and associations of other metallic and nonmetallic ores.

---

[1] Work on manuscript completed April 1960.
[2] Supervising metallurgist, Tuscaloosa Metallurgy Research Center, Bureau of Mines, Tuscaloosa, Ala.

Johannsen[3], Tomlinson[4], Sullivan[5], O'Meara and Clemmer[6], Krumbein and Pettijohn[7], and Clemmons, Stacy and Browning[8], have reported the use of heavy liquids for such purposes.

Among these investigators, Clemmons, and others, have discussed the application of sink-float techniques to sand separations. O'Meara and Clemmer[6] have discussed the various liquids used for separating high specific gravity minerals, and have presented methods for recovering and reclaiming the liquids.

As the O'Meara and Clemmer publication is no longer available, this report presents a compilation of more recent information regarding the properties of the different liquids commonly used. This report also discusses the sink-float techniques used in making sink-float separations. Because the liquids used in the higher specific gravity ranges are expensive, recovery and reclamation of the liquids for reuse also are discussed.

APPLICABILITY OF SINK-FLOAT SEPARATIONS

Sink-float separations can be made between minerals or rocks ranging from the lightest, such as pumice, expanded vermiculite, or perlite (which commonly have apparent specific gravities of less than 1), to minerals such as galena and others (specific gravity of 7.5 or greater). By an appropriate choice of liquid, or liquids, different minerals within a narrow range of specific gravities can be separated one from the other.

BASIC APPARATUS REQUIRED FOR LABORATORY SINK-FLOAT SEPARATIONS

Most sink-float fractionations can be carried out with a minimum of equipment. However, if many separations of extremely fine material are to be made, or if rapidity of separations is desired, the use of a centrifuge is helpful. The equipment usually used is as follows:

1. Several standard pear- or globe-shaped separatory funnels of about 250-milliliters that have a stopcock with a hole of at least one-quarter inch diameter. Special funnels for this purpose can be supplied by several laboratory glass manufacturers.

---

[3] Johannsen, Albert, Manual of Petrographic Methods: McGraw-Hill Book Co., 330 West 42nd St., New York, N.Y., 1918.

[4] Tomlinson, C. W., Method of Making Mineralogical Analysis of Sand: Trans. AIME, vol. 52, 1915, pp. 852-861.

[5] Sullivan, J. D., Heavy Liquids for Mineralogical Analysis: Bureau of Mines Tech. Paper 381, 1927, 26 pp.

[6] O'Meara, R. G., and Clemmer, J. B., Methods of Preparing and Cleaning Some Common Heavy Liquids used in Ore Testing: Bureau of Mines Rept. of Investigations 2897, 1928, 6 pp.

[7] Krumbein, W. C., and Pettijohn, F. J., Manual of Sedimentary Petrography: D. Appleton-Century Co., New York, N. Y., 1938.

[8] Clemmons, B. H., Stacy, R. H., and Browning, J. S., Heavy Liquid Techniques for Rapid Evaluation of Sands by Prospectors and Plant Operators: Bureau of Mines Rept. of Investigations 5340, 1957, 12 pp.

2. A funnel rack, several funnels, filter paper, and beakers of various sizes from 250-milliliter to 1,000-milliliter capacity. Fluted, 60° funnels of 75-millimeter diameter are satisfactory. A fast filtering, 15-centimeter diameter filter paper is recommended.

3. An inexpensive balance of 500-grams capacity, having an accuracy of about 0.1 gram is adequate for the usual sink-float applications.

4. A centrifuge equipped with eight 50-milliliter, conical heavy duty centrifuge tubes and capable of achieving a speed of at least 3,500 peripheral feet per minute, measured at tube end.

5. A polyethylene bottle for handy dispensing of the liquids and wash solutions.

6. Pans or containers for washing and drying the samples.

7. A hot plate for drying the samples.

Figure 1 shows the type of equipment used for laboratory sink-float separations and figure 2 gives a view of typical separations being carried out in beakers, separatory funnels, and centrifuge tubes.

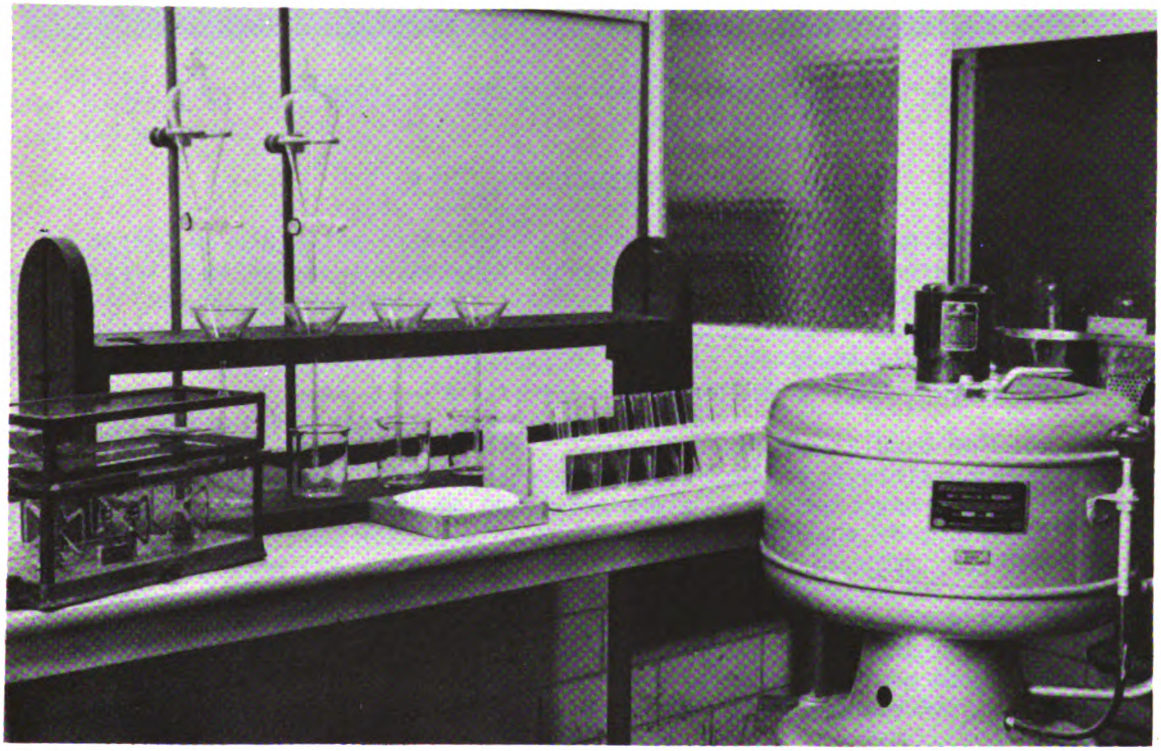

FIGURE 1. - Equipment for Laboratory Sink-float Separations.

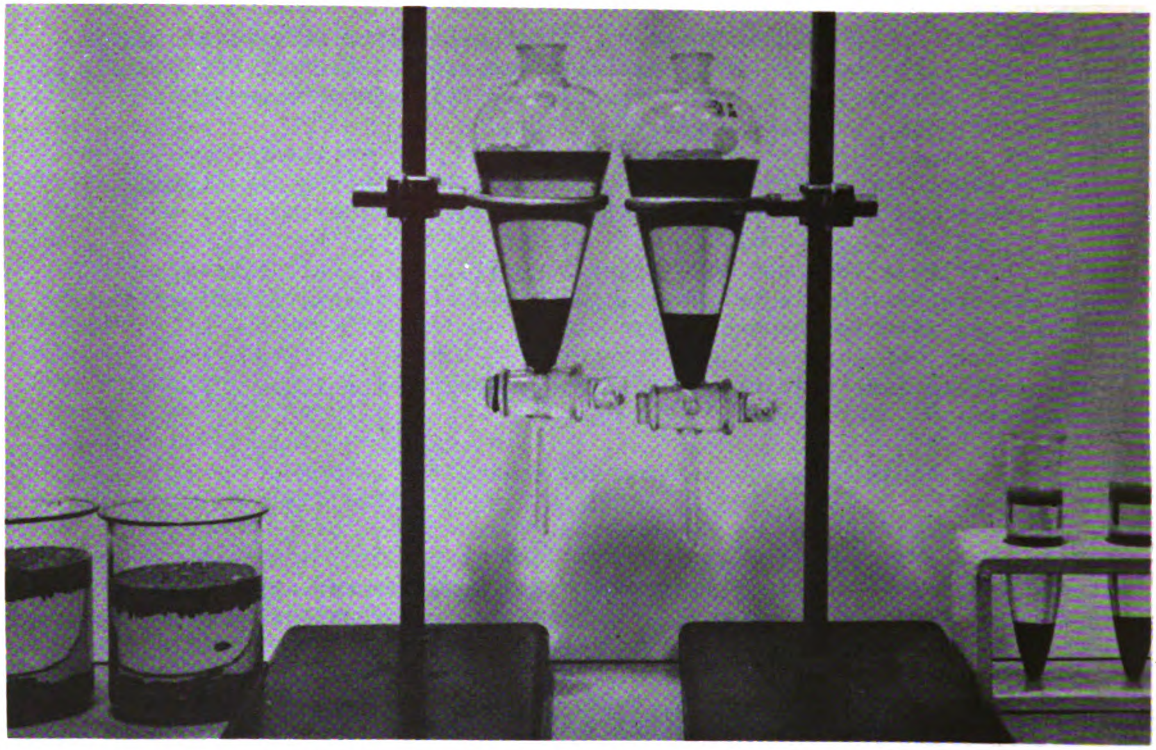

FIGURE 2. - Typical Sink-float Separations in Beakers, Separatory Funnels, and Centrifuge Tubes.

TEST PROCEDURES

Laboratory sink-float procedures can be applied to materials as coarse as 3 inches in diameter or as fine as 400-mesh. Separations of coarse materials can be carried out in beakers, whereas intermediate size samples may be fractionated in separatory funnels, thereafter, allowing the heavier fractions to settle and the lighter materials to float. Sizes finer than 200-mesh are best separated in separatory tubes using the centrifuge.

The liquids used in making sink-float separations should be recovered as completely as possible from the minerals by washing with a solvent. The chemicals are expensive and any residual liquids remaining on the grains will report as part of the weight of the mineral.

The samples to be separated by sink-float fractionation should be crushed or ground to a size assuring substantially complete liberation of the mineral components. In some instances the sample may be wet-ground in a pebble mill to insure liberation of the minerals, whereas in other instances crushing the ore to minus 2 or 3 inches may suffice.

The ground or crushed samples are usually washed free of slimes and clay by agitation with water followed by careful decantation. The sands are then dried, weighed, and the loss in weight recorded as "slime content". In some instances where the clay content is unusually high, the samples are subjected to attrition scrubbing in the presence of surface conditioners such as sodium hydroxide, sodium pyrophosphate, etc., to assure clean mineral surfaces. The scrubbing is usually accomplished by a 2- or 3-minute treatment in a laboratory conditioner or flotation cell. The samples (before sink-floating) are washed free of slime by careful decantation, followed by thorough drying, to avoid errors owing to moisture.

Beaker Separations

Materials coarser than 10-mesh usually are separated in beakers. The crushed rock or mineral mixtures are placed in a beaker together with the liquid of desired specific gravity, stirred, and then allowed to stand for a few minutes to permit the heavier minerals to sink and the lighter materials to float. The two layers are gently stirred to assure that any entrapped particles in either the sink or float fractions are freed and can seek their proper levels.

The float material is then skimmed from the top of the liquid and placed into a filter paper in one of the filter funnels, allowing the heavy liquid to drain off before washing. The sink material is washed from the beaker into a second filter funnel by using a polyethylene wash bottle of the heavy liquid. The liquid is allowed to drain off before washing. After draining both fractions, they are then washed with a solvent such as benzene, carbon tetrachloride, or acetone, added in three or four increments. After thorough washing, the products are dried and weighed.

Funnel Separations

Separatory funnels may be used for fractionating materials finer than 10- and coarser than 200-mesh. Usually, 50 to 60 grams of the sample are transferred to a 250-milliliter capacity separatory funnel containing 75 to 100 cubic centimeters of the liquid. The funnels are stoppered and swirled slowly to wet the samples thoroughly. The upper walls of the funnels are washed with a small quantity of heavy liquid to make sure that all of the mineral particles are wetted and washed into the body of the liquid.

Mineral particles having a specific gravity greater than that of the liquid will settle to the bottom of the funnel, whereas those having a specific gravity lighter than that of the liquid will float at the surface. After a period of time, depending upon the fineness of the material being treated, the mineral grains separate into two distinct layers. When the separation is observed, the funnel is again swirled carefully and gently to enable any mechanically entrapped particles in the sink or float fractions to migrate either upward or downward. The funnels are again allowed to stand for the formation of two distinct mineral layers. The sink product is then drawn off through the bottom of the separatory funnel through the stopcock onto a filter paper in one of the filter funnels, and the float fraction subsequently is transferred through the stopcock into a second filter funnel. If there is some question that the sink or float fractions contain entrapped gangue or mineral grains, the two fractions may be recleaned separately in other separatory funnels by using the procedures already described. After both fractions have been drained thoroughly of the liquid medium, they are washed with a solvent such as benzene, carbon tetrachloride or acetone, added in three or four increments. After washing, the float and sink fractions are dried, weighed, and the percent of sink and float are calculated.

Centrifuge Separations

Certain types of materials are more efficiently separated in the centrifuge than in beakers or separatory funnels. Generally, ores or mineral mixtures finer than 200-mesh, which tend to ball-up or to settle slowly, or samples containing needle-like minerals, such as spodumene or kyanite, are best fractionated in the centrifuge. The centrifugal force expedites settling of the fine materials and overcomes the tendency of the needle-like materials to form interlaced masses which either fail to settle out properly or cause entrapment of float material.

The general procedure employed in sink-float separation by centrifuging is much the same as when making the separation by settling techniques in the separatory funnel. Approximately 15 grams of the crushed rock or mineral sample is placed in a 50-milliliter conical tube together with 25 to 30-milliliters of the separating liquid. The samples are stirred with a small glass stirring rod, then the rod and sides of the tube are washed down, using a small quantity of the liquid. The tube then is placed in the centrifuge and whirled at a speed of about 3,500 to 4,000 peripheral feet per minute for a period of about 5 minutes. The tubes then are removed from the centrifuge and the stratified mineral layers again are stirred carefully with the rod to release mechanically entrapped particles. The tubes are replaced in the centrifuge and centrifuged for an additional 3 minutes to obtain a complete separation of the minerals. The sink and float fractions are removed from the centrifuge tubes, filtered to recover the liquid, and subsequently washed in the same manner described for the funnel procedure.

SINK-FLOAT LIQUIDS--THEIR PROPERTIES AND RECOVERY

Water

Our most abundant liquid, water, can be used for effecting separations between materials having an actual or apparent specific gravity lighter or heavier than 1. Water has been used for laboratory sink-float separations of expanded vermiculite[9] and has been similarly used in evaluation of expanded perlite.

Because it is abundant, no problems are involved in its recovery since the liquid can be discarded after use.

---

[9] McMillan, W. D., and Gerhardt, A. W., Investigation and Laboratory Testing of Vermiculite Deposits, Llano County, Tex.: Bureau of Mines Rept. of Investigations 4486, 1949, 42 pp.

Carbon Tetrachloride

Carbon tetrachloride is a commonly available volatile liquid having a specific gravity of 1.58 at 25° C. The chemical has a boiling point of 76.8° C. Carbon tetrachloride is miscible in all proportions with benzene yielding an infinite range of liquids having specific gravities between 0.88 and 1.58. Figure 3 shows the specific gravities of different mixtures of carbon tetrachloride and benzene.

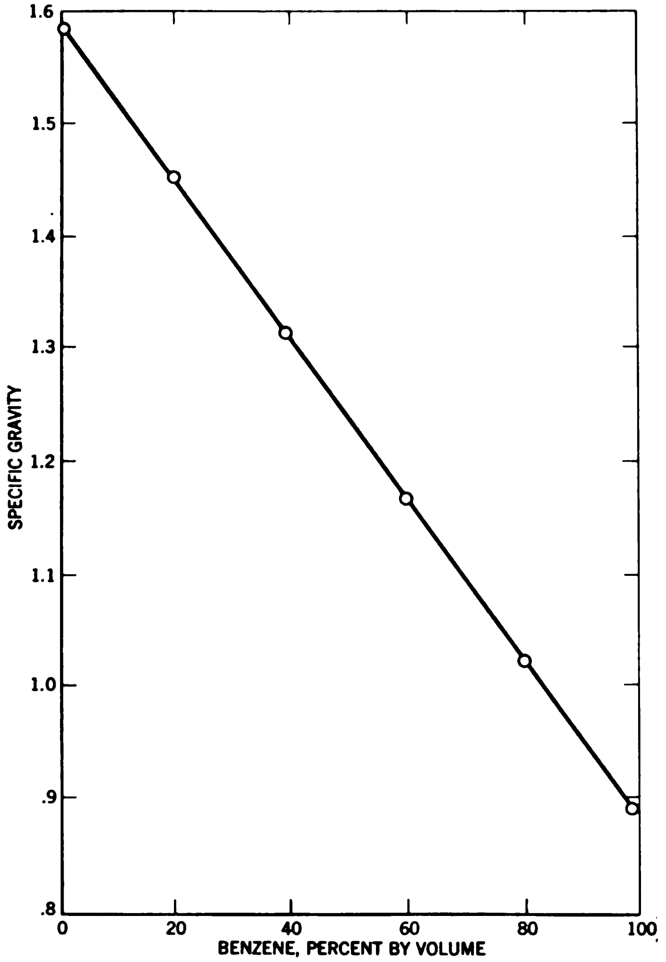

FIGURE 3. - Specific Gravity of Mixtures of Carbon Tetrachloride and Benzene at 25° C.

Except for its volatility, no particular problems are encountered in using carbon tetrachloride for mineral separations. When using the liquid, precautions should be taken to carry out the separations in a stoppered separatory funnel or covered beakers to prevent evaporation.

Both carbon tetrachloride and benzene are relatively cheap, and no effort is made to recover the liquid from the mineral grains after separation. The liquids remaining on the minerals are readily volatilized upon standing or by placing the ore samples on a warm hot plate.

Because of similar boiling points, the liquids are rarely separated after use, but instead are used as wash solutions in recovering the more expensive liquids used for separating minerals of heavier specific gravities.

Carbon tetrachloride and benzene are stable and they do not discolor. As a result, they can be used repeatedly.

Both carbon tetrachloride and benzene should be used in a well ventilated room and preferably under a hood, equipped with both updraft and downdraft ventilation.

Carbon tetrachloride is toxic by inhalation, prolonged or repeated contact of the liquid with the skin, or by ingestion. Benzene is highly volatile and flammable and the vapor is very toxic. The results of inhalation of the vapor are both acute and chronic. Acute poisoning results from the inhalation of vapors above 3,000 parts per million for even a few minutes.

Bromoform

Bromoform is a liquid at ordinary temperatures and has a specific gravity of 2.86 at 25° C. The chemical has a boiling point of 151° C. Normally, bromoform is used without dilution for the separation of minerals having specific gravities higher or lower than 2.86.

If separations at a specific gravity below 2.86 are desired, mixtures of bromoform and carbon tetrachloride can be used to give an infinite range of liquids having specific gravities between 2.86 and 1.58. Figure 4 shows the relationship between specific gravity and mixtures of bromoform and carbon tetrachloride.

Minerals separated in bromoform or a solution of bromoform and carbon tetrachloride are usually washed with carbon tetrachloride to recover the heavy liquid. The bromoform is concentrated from the dilute wash solutions by evaporating the carbon tetrachloride diluent. The carbon tetrachloride also may be recovered by fractional distillation. Usually, the washings from sink-float tests are allowed to stand in the open, under a hood. The diluent slowly evaporates until the bromoform returns to its original specific gravity.

While the bromoform is in use it becomes discolored owing to oxidation or contamination by the minerals being fractionated. Usually the addition of fuller's earth to the discolored liquid, followed by filtering, clarifies the bromoform. However, the liquid may have a red color after the fuller's earth treatment because of the presence of free bromine. The bromine is readily removed by shaking the liquid with a sodium or potassium hydroxide solution, separating the two liquids in a separatory funnel, and then drying the bromoform with calcium chloride.

The fumes from bromoform are mildly toxic and any separation involving its use should be carried out under a well ventilated hood.

Acetylene Tetrabromide

Acetylene tetrabromide is most widely used for making laboratory sink-float separations. When pure, the liquid is nearly colorless and has a specific gravity of 2.96 at 25° C. The liquid boils at 124° to 126° C. and is miscible in all proportions with either carbon tetrachloride or benzene.

Acetylene tetrabromide can be used without dilution for separating minerals having specific gravities higher or lower than 2.96. If mineral separations are required at specific gravities ranging from 1.58 to 2.96, mixtures of acetylene tetrabromide and carbon tetrachloride can be used.

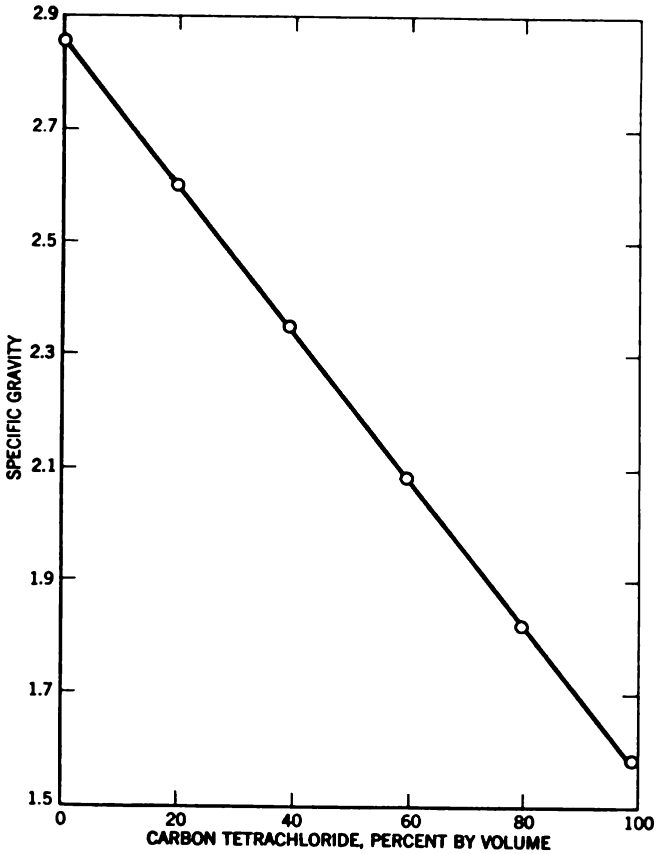

FIGURE 4. - Specific Gravity of Mixtures of Bromoform and Carbon Tetrachloride at 25° C.

The specific gravities of mixtures of acetylene tetrabromide and carbon tetrachloride are shown graphically in figure 5.

The acetylene tetrabromide adhering to the minerals after a sink-float separation is recovered by washing with carbon tetrachloride. The acetylene tetrabromide may be recovered from the wash solutions by evaporating or distilling off the carbon tetrachloride. Usually the washings are allowed to stand in the open, under a hood. The diluent evaporates slowly until the acetylene tetrabromide returns to its original specific gravity. Evaporation may be increased by warming the liquid or bubbling air through the solution. If heating is employed, care must be exercised to avoid overheating the solution as the tetrabromide will decompose. Decomposition of the acetylene tetrabromide causes the liquid to turn brown but does not impair its use for mineral separations other than lowering its specific gravity slightly.

Discolored acetylene tetrabromide may be cleaned by agitating it in a separatory funnel with a small quantity of bromine until the mixture assumes a deep red color, followed by addition of a small quantity of sodium hydroxide and continued agitation. After standing, the decolorized acetylene tetrabromide and the caustic solution separate. The acetylene tetrabromide can be withdrawn from the bottom of the funnel, dehydrated by adding calcium chloride and then filtered to remove the calcium chloride.

Fumes of acetylene tetrabromide are toxic and any separations involving use of the liquid should be carried out under a well ventilated updraft and downdraft hood. Acetylene tetrabromide may be purchased for about 65 cents per pound (1959).

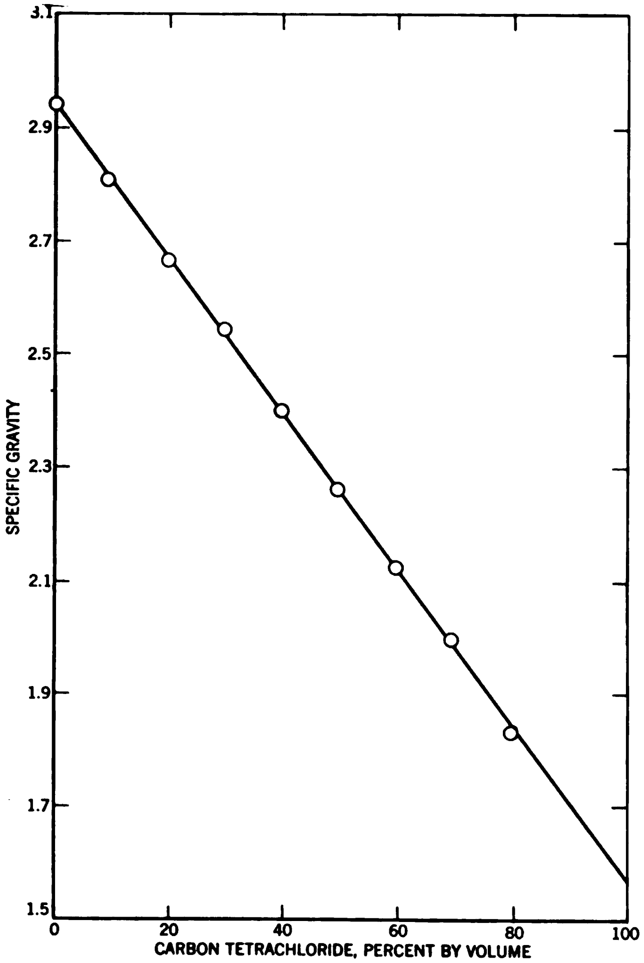

FIGURE 5. - Specific Gravity of Mixtures of Acetylene Tetrabromide and Carbon Tetrachloride at 25° C.

Methylene Iodide

Pure methylene iodide has a light straw color and a specific gravity of 3.32 at 25° C. The chemical boils at 180° C. The high cost of methylene iodide, which was about $15 per pound (1959), is a deterrent to its popular usage. Consequently, other more readily recoverable liquids are usually used in its stead. However, in some sink-float separations where a liquid of 3.32 specific gravity is desired, methylene iodide is used undiluted.

Methylene iodide is recovered from the mineral particles by washing with carbon tetrachloride which may be removed from the wash solutions by evaporation under a hood. Heating the wash solutions to facilitate evaporation of the carbon tetrachloride should be avoided as methylene iodide decomposes readily.

In use or exposure to strong light, methylene iodide slowly decomposes, liberating iodine which causes the liquid to turn red. The normal straw color may be restored by agitating with a dilute solution of sodium or potassium hydroxide, separating the decolorized liquid, drying with calcium chloride, and filtering. Methylene iodide also may be decolorized by shaking with a few drops of mercury. The liquid should be stored in the dark with a few beads of metallic copper added to prevent discoloration.

Thallium Formate

Thallium formate is a metal-organic, water soluble salt. A saturated solution of the salt at 90° C. has a specific gravity of 5. Water solutions of the salt are normally used for sink-float separations in a specific gravity range of 2.95 to 3.5. The specific gravity of different mixtures of thallium formate and water at 90° C. is shown in figure 6.

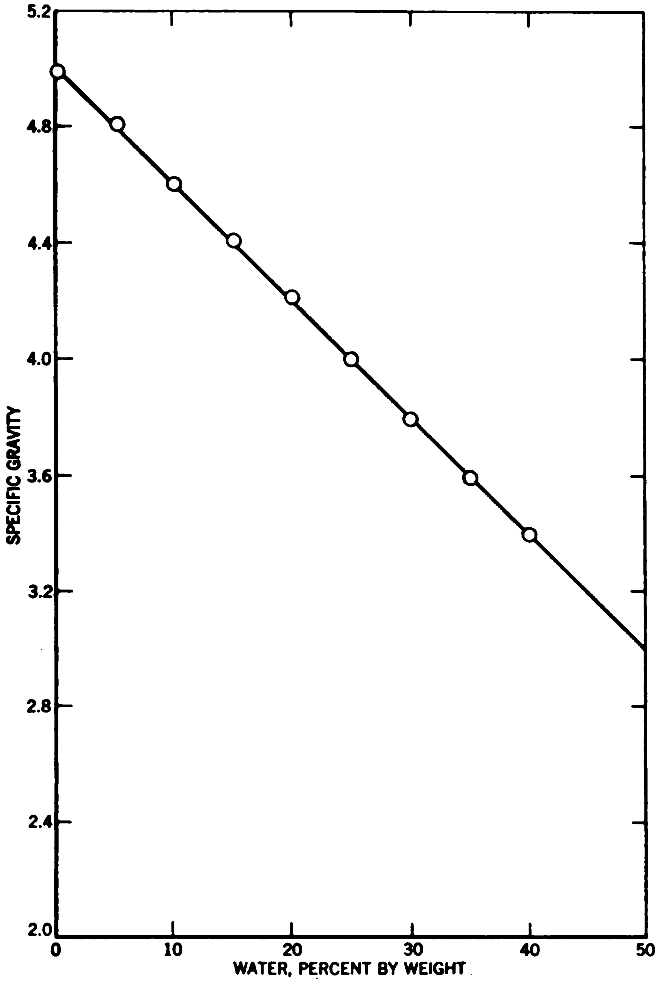

FIGURE 6. - Specific Gravity of Mixtures of Thallium Formate and Water at 90° C.

When used for sink-float separations, the thallium formate is recovered by washing the mineral grains with hot distilled water. The formate salt is then recovered from the wash solutions by evaporating the water. After standing for any length of time, a black or brown residue may form in the wash solutions. The residue is easily dissolved by: (1) adding a small quantity of formic acid, evaporating the solution just to dryness to volatilize any free formic acid, (2) redissolving the solids in a small quantity of distilled water and again evaporating to dryness. Care must be taken not to evaporate the solution at a temperature above 130° C., as the chemical will decompose.

Thallium formate is extremely toxic and poisonous to the touch. The chemical can be readily absorbed through the skin, and can cause widespread damage to the nervous system, kidneys, digestive tract and circulatory system. Personnel using thallium formate should be extremely cautious. The recommended precautions are, use of a respirator to avoid inhaling the material, protective clothing and rubber gloves to avoid skin contact and absorption, and safety goggles for protection of the eyes. Any person handling thallium formate should be given detailed instructions regarding its proper use.

The cost of thallium formate was about $10.50 per 100 grams (1959).

Thallium-Malonate-Formate

Thallium-malonate-formate is a mixture of thallium formate and thallium malonate salts. At ordinary room temperatures the double salt dissolves in water to yield a saturated solution, known as Clerici's solution, having a specific gravity of 4.25. Clerici's solution is used in making sink-float separations in the specific gravity range of 3.5 to about 5. The specific gravities of mixtures of thallium-malonate-formate and water at 90° C. are shown graphically in figure 7.

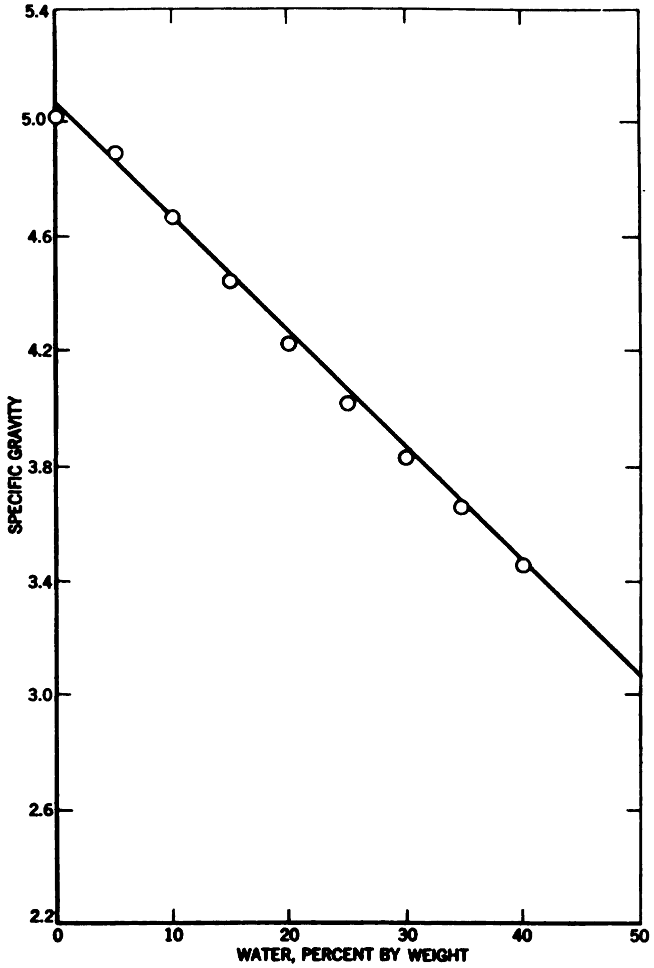

FIGURE 7. - Specific Gravity of Mixtures of Thallium-malonate-formate and Water at 90° C.

Generally, Clerici's solution is used at temperatures slightly higher than room temperature. Only where high specific gravities are desired are hot saturated solutions used. When separations are made in beakers, the temperature of the solution is readily maintained by placing the beaker on a sand bath. When using separatory funnels, the funnel may be wrapped with a heating element and the temperature thermostatically controlled.

The double salt is recoverable from minerals by washing with water. The salt is reclaimed from the wash solutions and purified in the same manner as thallium formate.

Thallium-malonate-formate is extremely poisonous and it must be handled with the same care as thallium formate.

Thallium-malonate-formate costs about $7.85 per 100 grams (1959).

Cargille Heavy Liquids

The Cargille heavy liquids[10] are a new group of liquids for effecting sink-float separations at specific gravities ranging between 3.6 and 7.5. The liquids are suspensions of heavy metals dispersed in heavy liquid liquids, and are used in much the same manner as the lower specific gravity liquids. The use of Cargille liquid is limited to the sink-float separation of coarse mineral grains, usually larger than 28-mesh in size. The Cargille liquids can be obtained in a suite, each liquid of which increases in specific gravity by a constant increment. The heavy metals in Cargille liquids settle slowly and form a soft mass at the bottom of the material. Before use, the suspension must be stirred to disperse the metal uniformly throughout the liquid.

---

[10] Wagner, E. R., Cargille Heavy Liquids: Circular 53-HLM, R. P. Cargille Laboratories, Inc., New York 6, N. Y.

The Cargille liquid adhering to the minerals after separation can be removed by washing with the common solvents. The liquid is recovered by evaporation of the solvent in the same manner used for the other organic liquids.

The Cargille liquids should be used with good ventilation in an updraft and downdraft hood. Care should be exercised not to breathe the fumes or to allow contact with the skin.

At the present time, Cargille heavy liquids are used primarily for making specific gravity determinations of large mineral particles above the range of Clerici's solution.

DIFFICULTIES ENCOUNTERED IN SINK-FLOAT SEPARATIONS

Mineral separations are often incomplete or imperfect for the following reasons:

1. Convection currents in the separating liquid.
2. Entrapment of mineral grains of one gravity in the sink or float fraction of another gravity.
3. Interlocking of mineral grains of different specific gravities.
4. Presence of alteration products on the minerals which cause the density of a mineral to differ from theoretical specific gravity.
5. Extreme fineness of the material which results in "balling up" or slow settling.
6. Small differences in specific gravity between the minerals and the heavy liquid.

Careful control of temperature will prevent convection currents in the liquids, whereas repeated separations or frequent stirring will usually overcome the incomplete separation caused by entrapment. The settling rate of very fine mineral grains or grains approaching the specific gravity of the liquid may be accelerated by centrifuging.

SAFETY PRECAUTIONS FOR HANDLING SINK-FLOAT LIQUIDS

Except for water, all of the sink-float liquids are toxic and hazardous in varying degrees. The sink-float separations should always be made under a hood equipped with both updraft and downdraft ventilation. The fumes of the liquids should not be breathed or allowed to contact the skin. For more information regarding the toxicity of the liquids discussed in the text, Sax[11] should be consulted. The toxicity and hazards of the liquids and the first aid treatment to be applied in event of exposure or contact with the liquids are discussed.

---

[11] Sax, N. Irving, Handbook of Dangerous Materials: Reinhold Publishing Corporation, 330 W. 42nd St., New York 18, N. Y., 1951, 848 pp.

* U.S. GOVERNMENT PRINTING OFFICE : 1961 O—582799